The Crystal Structures of Bis(*cis*-1,3-diaminocyclohexane)palladium(II) Chloride and Its Platinum(II) Analogue

Keiko KAMISAWA, Keiji MATSUMOTO, Shun'ichiro OOI,* Hisao KUROYA,
Reiko SAITO,** and Yoshinori KIDANI***
Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi-ku, Osaka 558
***Aichi Junior College of Nursing, Kamishidanmi, Moriyama-ku, Nagoya 463*
***Faculty of Pharmaceutical Sciences of Nagoya City University, Tanabedori, Mizuho-ku, Nagoya 467*

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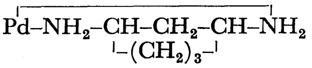
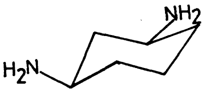
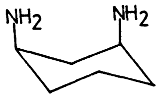
The structure of bis(*cis*-1,3-diaminocyclohexane)palladium(II) chloride has been determined from X-ray diffraction data collected by the counter method. The crystal is orthorhombic with space group Pnnm, $a=17.728(5)$, $b=6.418(4)$, $c=6.914(2)$ Å, and $Z=2$. The crystal structure has been determined by Patterson and Fourier techniques and refined by a least-squares method to $R=0.026$ for 1151 independent reflections for which $F_o^2>3\sigma(F_o^2)$. The Pd atom has a planar coordination of 4 N atoms and the complex cation has a crystallographically imposed C_{2h} symmetry, the two *cis*-1,3-diaminocyclohexane ligands being related to each other by a two fold axis. The six-membered chelate ring  $\mathrm{Pd{-}NH_2{-}CH{-}CH_2{-}CH{-}NH_2}$ (with $\mathrm{-(CH_2)_3-}$ linking the two CH) is of the envelope conformation. The structural features of the ligating *cis*-1,3-diaminocyclohexane have been described. The crystal of bis(*cis*-1,3-diaminocyclohexane)platinum(II) (orthorhombic, $a=17.727(8)$, $b=6.371(3)$, $c=6.965(2)$ Å) was found to be isomorphous with that of the palladium analogue.

The *cis*-1,3-diaminocyclohexane (1,3-dach) molecule usually exists in the diequatorial conformation in which the disposition of the two NH_2 groups is highly unfavorable to chelation. However, the molecule is capable of chelating to the metal ion when it assumes the diaxial conformation.



The diequatorial conformation



The diaxial conformation

Two of the authors (R. S. and Y. K.) have found that 1,3-dach reacts with some transition metal ions and have synthesized several Pd(II) and Pt(II) chelates of 1,3-dach with the formula $[MX_2(1,3\text{-dach})]$ and $[M(1,3\text{-dach})_2]Cl_2$, where M stands for Pd(II) or Pt(II) and X for Cl or Br.[1] Thus the presence of a metal ion which has a strong affinity towards the N atom promotes the interconversion from the diequatorial to the diaxial conformation, giving rise to a metal chelate of 1,3-dach. With these complexes it was found that the electronic spectra were indicative of a planar 4-coordinate configuration, and furthermore, the ^1H NMR and IR spectra suggested the diaxial conformation of the 1,3-dach ligand. In order to investigate the structural features of the ligating 1,3-dach molecule in detail, the single crystal X-ray structure analysis of $[Pd(1,3\text{-dach})_2]Cl_2$ has been performed.

Experimental

The preparations of $[Pd(1,3\text{-dach})_2]Cl_2$ and $[Pt(1,3\text{-dach})_2]Cl_2$ have been reported elsewhere.[1]

Crystal Data. *[Pd(1,3-dach)₂]Cl₂*: $C_{12}H_{28}N_4Cl_2Pd$, *F.W.*$=405.7$, Orthorhombic, $a=17.728(5)$, $b=6.418(4)$, $c=6.914(2)$ Å, $U=786.7(6)$ Å^3, $D_m=1.71$, $D_c=1.71$ g/cm^3, $Z=2$, $\mu(\text{Mo }K\alpha)=16.1$ cm^{-1}, space group Pnnm or Pnn2 from systematic absences: $h0l$ when $h+l$ is odd, $0kl$ when $k+l$ is odd. The former space group was used in the structure analysis and confirmed by the successful refinement of the structure.

[Pt(1,3-dach)₂]Cl₂: $C_{12}H_{28}N_4Cl_2Pt$, *F.W.*$=494.4$, Orthorhombic, $a=17.727(8)$, $b=6.371(3)$, $c=6.965(2)$ Å, $U=786.7(3)$ Å^3, $D_m=2.08$, $D_c=2.09$ g/cm^3, $Z=2$, $\mu(\text{Mo }K\alpha)=105.6$ cm^{-1}, space group Pnnm or Pnn2; X-ray diffraction pattern showed the same space-group extinctions as those of the Pd analogue.

The Laue symmetries, space groups, and the approximate unit-cell dimensions were determined from oscillation and Weissenberg photographs taken with Cu $K\alpha$ radiation. The unit cell dimensions of the respective compounds were refined by the least-squares analyses of the θ values (16 reflections for the Pd- and 14 for the Pt-compound) measured on a Philips PW 1100 four-circle diffractometer with Mo $K\alpha$ radiation.

Data Collection. Intensity data for one octant of the reciprocal space were collected by the ω-2θ scan technique with graphite-monochromated Mo $K\alpha$ radiation. The specimen size was $0.14\times0.12\times0.15$ mm. A scan speed of 0.017° s^{-1} in ω and a scan range $(0.8+0.2\tan\theta)°$ were chosen. The background was counted for half of the scan time at each end of the scan range. Three standard reflections (200, 040, 002), monitored every 3 h throughout the data collection, showed no significant variation in intensity. Of the 1752 reflections collected in the range of $2\theta\leq66°$, 1151 reflections having $F_o^2>3\sigma(F_o^2)$ were used in the structure analysis. Intensity data were processed by the computer program of Hornstra and Stubbe.[2] A spherical absorption correction ($r=0.07$ mm) was applied.

Structure Determination and Refinement. The crystal structure of $[Pd(1,3\text{-dach})_2]Cl_2$ was solved by the heavy-atom technique. Of the two possible space groups, Pnnm and Pnn2, the former was chosen. The positional and thermal parameters were refined by the block-diagonal least-squares method. The minimized function was $\sum w(|F_o|-|F_c|)^2$. The weighting scheme, $w=p$ for $|F_o|<F_{\min}$, $w=1.0$ for $F_{\min}\leq|F_o|\leq F_{\max}$, and $w=(F_{\max}/F_o)^2$ for $|F_o|\geq F_{\max}$, was used. The p, $F_{\min}$ and $F_{\max}$ were varied as indicated by F_o and $(\sin\theta/\lambda)$ analysis of $\sum w\,\Delta F^2$. The difference Fourier map, calculated after the refinement of the parameters for the nonhydrogen atoms by the use of anisotropic temperature factors, clearly showed the peaks of all H atoms. These H atoms were

TABLE 1. POSITIONAL AND THERMAL PARAMETERS

Atomic coordinates ($\times 10^4$).

	x	y	z
Pd	0	0	0
Cl	4129.9(5)	2313(1)	0
N	575(1)	1481(3)	2191(3)
C(1)	1971(2)	−134(6)	0
C(2)	1954(1)	1218(4)	1806(4)
C(3)	1282(1)	2696(4)	1847(4)
C(4)	1220(2)	3972(5)	0

Anisotropic temperature factors ($\times 10^4$) in the form $\exp[-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)]$.

	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Pd	12.62(7)	136.7(6)	78.3(4)	6.6(6)	0	0
Cl	22.5(2)	163(2)	146(2)	−32(1)	0	0
N	16.3(5)	175(5)	98(3)	7(3)	0000(2)	−39(7)
C(1)	16.5(7)	116(7)	129(5)	26(5)	0	0
C(2)	16.5(6)	163(5)	125(5)	2(3)	−12(3)	−5(9)
C(3)	18.7(6)	135(5)	127(4)	−1(3)	−3(3)	−71(8)
C(4)	24.3(11)	101(7)	197(9)	5(5)	0	0

Atomic coordinates ($\times 10^3$) and isotropic temperature factros of H atoms.

	x	y	z	$B/\text{Å}^2$
H(1N)	25(1)	222(5)	275(5)	3.1(7)
H(2N)	66(2)	49(4)	305(5)	2.7(7)
H(1C1)	153(2)	−115(7)	0	2.4(9)
H(2C1)	244(2)	−95(7)	0	2.6(9)
H(1C2)	240(2)	206(4)	180(5)	3.0(7)
H(2C2)	193(1)	40(4)	298(5)	2.8(7)
H(C3)	133(1)	359(4)	295(4)	2.3(6)
H(1C4)	79(3)	472(7)	0	3.3(10)
H(2C4)	163(2)	490(7)	0	3.0(10)

included in the following least-squares calculation, isotropic temperature factors being used. The convergence was attained at R 0.026 ($R'=[\sum w\Delta F^2/\sum wF_o^2]^{1/2}=0.030$). In the final cycle of the refinement all parameter shifts were less than 0.2σ. The $F_{\text{min}}=8.7$, $F_{\text{max}}=42.0$ and $p=0.4$ were found to be optimum.

The atomic scattering factors of Pd^0, Cl$^-$, N, and C were taken from Ref. 3 and that of H from Ref. 4. Real parts of the anomalous dispersion corrections were applied for Pd^0 and Cl$^-$. Atomic coordinates and temperature factors are given in Table 1. A complete list of the observed and calculated structure factors is preserved by the Chemical Society of Japan (Document No. 7823). All the computations were carried out on a FACOM 230-60 computer of Osaka City University, by the use of the RSSFR-5, HBLS-IV, and DAPH programs in the UNICS.[5]

Results and Discussion

The perspective drawing of the complex cation is shown in Fig. 1. The complex has a crystallographically imposed two fold axis and a symmetry plane; the two fold axis runs through the Pd atom and bisects the N–Pd–N″ angle, whereas the symmetry plane is perpendicular to the two fold axis and passes through the Pd, C(1) and C(4) atoms. The primed atoms are related to the unprimed ones by the symmetry plane. Thus the complex has an exact C_{2h} symmetry, the Pd atom being located at the center of inversion.

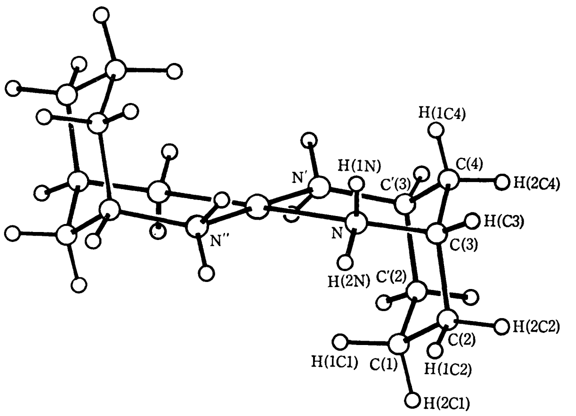


Fig. 1. Structure of $[\text{Pd}(1,3\text{-dach})_2]^{2+}$.

The six-membered chelate ring composed of the Pd, N, C(3), C(4), C′(3), and N′ is of the envelope conformation. However, the [Pd, N, N′] plane is not exactly coplanar with the [N,C(3),C′(3),N′] plane; as can be seen in the elevation of the complex (Fig. 2), the latter plane is slightly bent away from the former plane so as to deform the chelate ring toward the chair conformation. The interplanar angle is 169.2° (Table 3).

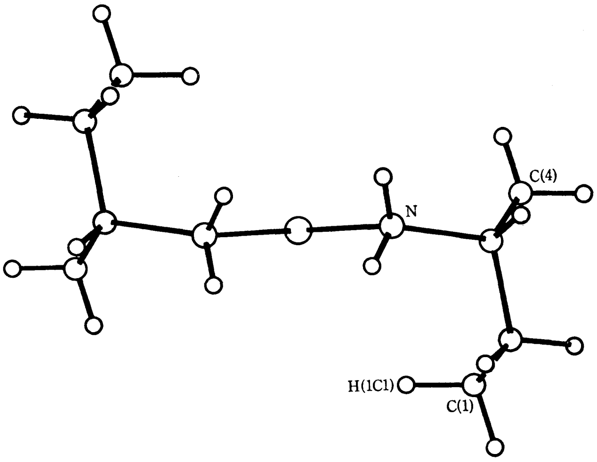


Fig. 2. Elevation of $[\text{Pd}(1,3\text{-dach})_2]^{2+}$.

Bond lengths and angles are given in Table 2. The Pd–N bond length (2.058(2) Å) is slightly longer than those in $[\text{Pd(en)}_2]\text{Cl}_2$ (2.030(6) and 2.043(7) Å),[6] $[\text{PdCl}_2(\textit{meso}\text{-2,3-diaminobutane})]$ (2.029(6) Å),[7] and $[\text{Pd}(N^1\text{-Me-}(S)\text{-pn})_2]\text{Cl}_2\cdot 2\text{H}_2\text{O}$ (2.040(5) Å),[8] although the magnitude of elongation is not "highly significant." The electronic spectra of the present complex shows two bands at 27000 cm^{-1} (shoulder) and 34200 cm^{-1}.[1] These bands are displaced slightly to a lower energy relative to the corresponding bands of $[\text{Pd}(R\text{-pn})_2]\text{Cl}_2$ (29000 and 34800 cm^{-1}).[9] As the Pd–N bond length in the *R*-pn complex should presumably not be different from those in the en and *meso*-2,3-diaminobutane complexes, the slight elongation of the Pd–N bond in the 1,3-dach complex seems to be responsible for the low energy shift of the d→d bands.

Table 2. Interatomic distances (l) and bond angles (ϕ)

	l/Å		ϕ/°
Pd–N	2.058(2)	N–Pd–N′	94.8(2)
N–C(3)	1.494(3)	Pd–N–C(3)	122.6(2)
C(1)–C(2)	1.521(5)	C(2)–C(1)–C′(2)	110.4(4)
C(2)–C(3)	1.523(4)	C(1)–C(2)–C(3)	112.7(2)
C(3)–C(4)	1.521(5)	C(2)–C(3)–C(4)	112.1(2)
		C(3)–C(4)–C′(3)	114.2(4)
C(2)···C′(2)	2.497(5)	N–C(3)–C(4)	110.8(2)
C(3)···C′(3)	2.554(5)	N–C(3)–C(2)	109.5(2)
N···N′	3.029(4)		
N–H(1N)	0.84(3)	H(1C1)–C(1)–H(2C1)	108(4)
N–H(2N)	0.89(3)	H(1C1)–C(1)–C(2)	111(2)
C(1)–H(1C1)	1.02(4)	H(2C1)–C(1)–C(2)	109(2)
C(1)–H(2C1)	0.99(4)	H(C3)–C(3)–N	105(2)
C(2)–H(1C2)	0.95(3)	H(C3)–C(3)–C(2)	109(2)
C(2)–H(2C2)	0.97(3)	H(C3)–C(3)–C(4)	110(2)
C(3)–H(C3)	0.96(3)	H(1C4)–C(4)–H(2C4)	108(4)
C(4)–H(1C4)	0.90(4)	H(1C4)–C(4)–C(3)	110(3)
C(4)–H(2C4)	0.94(4)	H(2C4)–C(4)–C(3)	107(3)
Pd···H(1C1)	2.81(4)	Pd···H(1C1)–C(1)	125(3)
Pd···H(1C4)	3.34(4)	Pd···H(1C4)–C(4)	83(3)
N···Cl*[a]	3.347(2)		
H(2N)···Cl*	2.47(3)	Cl*···H(2N)–N	170(3)
N″···Cl*	3.307(2)		
H(1N″)···Cl*	2.54(3)	Cl*···H(1N″)–N″	152(3)

a) The Cl* denotes the chloride anion at the equivalent position ($1/2-x, y-1/2, 1/2+z$).

Table 3. Interplanar and torsion angles

Interplanar angles (ϕ)

Plane (1)	Pd, N, N′
Plane (2)[a]	N, C(3), C′(3), N′
Plane (3)	C(3), C(4), C′(3)
Plane (4)[a]	C(2), C(3), C′(3), C′(2)
Plane (5)	C(2), C(1), C′(2)

Plane	Plane	ϕ/°
(1)	(2)	168.9
(2)	(3)	114.4
(2)	(4)	109.6
(3)	(4)	136.1
(5)	(4)	130.5

Torsion angles (τ)

Fragment	τ/°
Pd–N–C(3)–C(4)	40.9
Pd–N–C(3)–C(2)	−83.3
N–C(3)–C(2)–C(1)	71.2
N–C(3)–C(4)–C′(3)	−74.2
C′(2)–C(1)–C(2)–C(3)	55.6
C(1)–C(2)–C(3)–C(4)	−52.1
C(2)–C(3)–C(4)–C′(3)	48.5

a) All four atoms lie exactly on one plane.

The N–Pd–N′ bond angle (94.8(2)°) is significantly larger than those in the Pd complexes with five-membered chelate rings of diamines (82.9—83.6°).[6–8] Although the Pd–N–C bond angle (122.6(2)°) is fairly larger than the tetrahedral angle, it is comparable to those in the metal chelates with six-membered chelate rings.[10]

The cyclohexane ring is of the diaxial conformation, as inferred from ^{1}H NMR and IR spectra.[1] Bond lengths and angles are in reasonable agreement with those in the cyclohexane II,[11] *trans*-1,2-diaminocyclohexane,[12] and *trans*-1,4-diaminocyclohexane.[13] However, the C(3)–C(4)–C′(3) bond angle (114.2(4)°) is larger than any C–C–C angles (≈112.3°) in the molecules cited for comparison.

Various torsion angles are also given in Table 3. The torsion angles of the –C–C–C–C– fragments are generally smaller than those in the cyclohexane and its substituted derivatives (55.4—58.4°)[11–13] and particularly, that of the –C(2)–C(3)–C(4)–C′(3)– is the smallest (48.5°) among them. This value is comparable to that (47.0°) found in the $-CH_2-CH(COOH)-CH(COOH)-CH_2-$ portion of the *trans*-1,2-cyclohexanedicarboxylic acid,[14] the small value of which has been ascribed to the steric repulsion between the two carboxyl groups.[15] Interpretation for the present case of –C(2)–C(3)–C(4)–C′(3)– is as follows. In the scaled model of the diaxial 1,3-dach molecule, the distance between N and N′ is 2.7 Å[16] (the same atom numbering as the one given for coordinating 1,3-dach (Fig. 1) is used for the scaled model but expressed in bold-faced type). In order to increase the **N**···**N′** distance to 3.029 Å as found in the present 1,3-dach ligand it is necessary to synchronously rotate the $-\mathbf{C}(\mathbf{3})\begin{smallmatrix}\diagup\mathbf{N}\\ \diagdown\mathbf{C}(\mathbf{4})\end{smallmatrix}$ and $-\mathbf{C}'(\mathbf{3})\begin{smallmatrix}\diagup\mathbf{C}(\mathbf{4})\\ \diagdown\mathbf{N}'\end{smallmatrix}$ segments about **C**(**2**)–**C**(**3**) and **C′**(**2**)–**C′**(3) axes, respectively. Such rotations give rise to i) decrease of torsion angle in the –**C**(**2**)–**C**(**3**)–**C**(**4**)–**C′**(**3**)– fragment, ii) increase of the interplanar angle between [**C**(**2**), **C**(**3**),**C′**(**3**),**C′**(**2**)] and [**C**(**3**),**C**(**4**),**C′**(**3**)] planes, and iii) increase of **C**(**3**)–**C**(**4**)–**C′**(**3**) bond angle. Actually, in ligating 1,3-dach the corresponding interplanar angle is larger by 5.6° than the [C(2),C(3),C′(3),C′(2)]–[C(2),C(1),C′(2)] interplanar angle which is in agreement with the average value in cyclohexane II (130.3°). Moreover, the C(3)–C(4)–C′(3) bond angle is the largest among the C–C–C bond angles. In the intermolecular contacts in which the H atoms of the cyclohexane group participate, none of the interatomic distances is less than the sum of the van der Waals

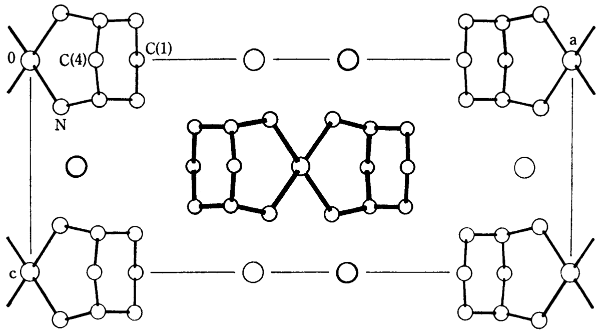


Fig. 3. Crystal structure viewed down the b axis. Complexes drawn by thin lines lie at $y=0$, while that shown by thick lines is located at $y=1/2$. For Cl anions thin circles have $y\approx0.23$, and thick ones $y\approx0.73$.

radii. Therefore, the structural features of the cyclohexane ring found in ligating 1,3-dach should be regarded as arising from an intramolecular potential energy but not from an intermolecular one.

Figure 3 shows the crystal structure. All H atoms of the NH_2 groups participate in the N–H···Cl hydrogen bonding. Data concerning the hydrogen bonds are listed in Table 2.

The unit-cell dimensions of $[Pt(1,3\text{-dach})_2]Cl_2$ are very close to those of $[Pd(1,3\text{-dach})_2]Cl_2$ and furthermore, the intensity distribution in the reciprocal space of the former has similar features to that of the latter. Accordingly the crystal in the former case may be regarded as isomorphic with the present Pd compound.

The H(1C1) atom has a short contact with the Pd atom. The Pd···H distance is comparable with that found in the bis(L-ornithinato)palladium(II) (2.79 Å).[17] In the ^1H NMR spectrum of the $[Pt(1,3\text{-dach})_2]Cl_2$ it was found that one of the eight methylene protons resonates at lower field than those for the remainders. The spectrum of the Pd analogue is almost identical with that of the Pt complex.[1] The proton which shows down-field shift is thought to be the H(1C1) atoms, although in solution the M···H distance varies as the ligand molecules make some motion, *e.g.*, the rapid oscillation of the 1,3-dach ligand about N···N′ axis.

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16) The coordinates of C atoms in the cyclohexane II[11] were utilized in the estimation of the N···N′ distance in the scaled model. The coordinates of the two axial N atoms, each of which is bonded to C(2) or C′(1) atom of the cyclohexane II (C′(1), C(1) at equivalent position $1/2-x, 1/2-y, -z$), were calculated on the assumption that the C–N bond length is 1.494 Å and each C atom has sp^3 hybridization with C_{2v} symmetry. From such a model the N···N′ distance was calculated to be 2.68 Å.

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